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Boatz 5364

Christe 5194

AFOSR Molecular Dynamics Contractors Conference **(Statement A)**
(San Diego, CA, 18-20 May 2003) (Deadline: 18 May 2003)

Towards New Polynitrogen Species: The Search for Viable Precursors

AFOSR Molecular Dynamics Contractors Conference
May 18-20, 2003

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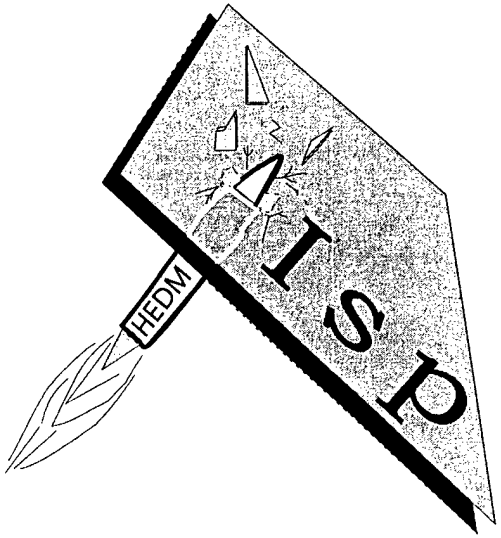
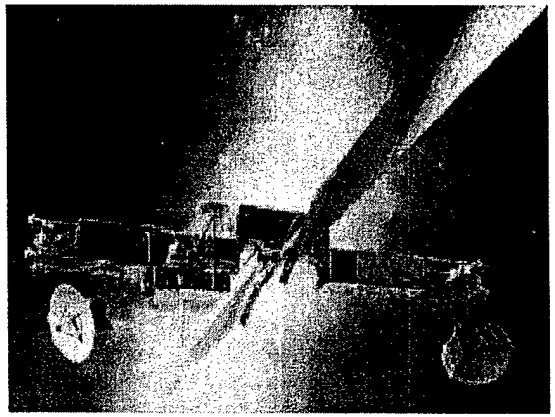
HEDM Program Objective

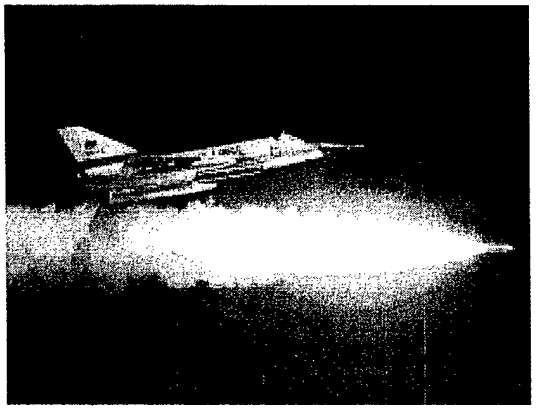


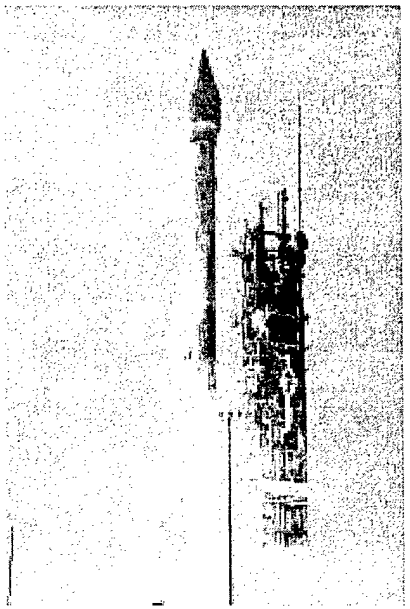
Breaking the performance barrier

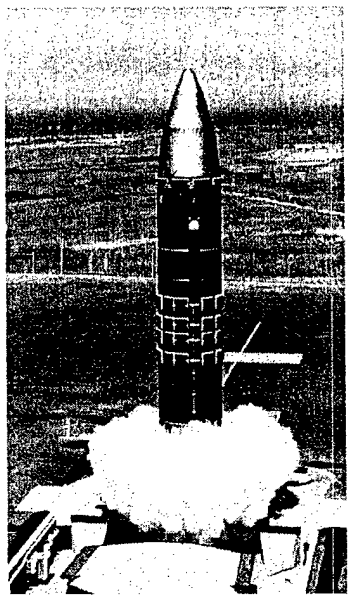
Identify and develop advanced chemical propellants for rocket propulsion applications

- **Hydrocarbons for liquid boosters**
- **Liquid & solid oxidizers for boost and upper stages**
- **Monopropellants for upper stages and satellites**









Current State of the Art

Monopropellants	Isp (sec)	Density (g/cm^3)
Hydrazine (N_2H_4)	200	1.01
Hydrogen Peroxide (H_2O_2)	175	1.41
Solids		
Ammonium Perchlorate (AP)	260	1.69
~20%Al/~10% polymer binder		
Liquids		
N_2O_4/Hydrazine	280	1.45/1.01
RP-1/Liquid Oxygen (LOX)	300	0.81/1.15
Cryogenic		
Liquid Hydrogen (LH2)/LOX	390	0.07/1.15

I_{sp} at sea level 1000 psi chamber pressure

Isp = (pounds of thrust/pounds of propellant/second)

HEDM Propellant Payoffs

"The highest leverage technology area impacting launch vehicles is the development of high-energy-density materials for use as propellants."
-- New World Vistas Panel on Space Technology (1995)

Vehicle Type	Baseline Vehicle	Propellant	Takeoff Mass (lb)	Payload Mass (lb)	Payload Mass (lb) With 10% Isp Increase
Two-stage ELV	Atlas II // Centaur D-1A	RP-1/LOX (Isp = 295 s) // LH2/LOX (Isp = 455 s)	360,000	12,500	15,600 **(+25%)**
SSTO RLV	Lockheed SSTO	LH2/LOX (Isp = 455 s)	1,900,000	40,000	68,000 **(+70%)**
Missile Defense Interceptor	Boost-Phase Interceptor	HTPB/Al/HMX (Isp = 270 s)	1,847	74	110 **(+49%)**

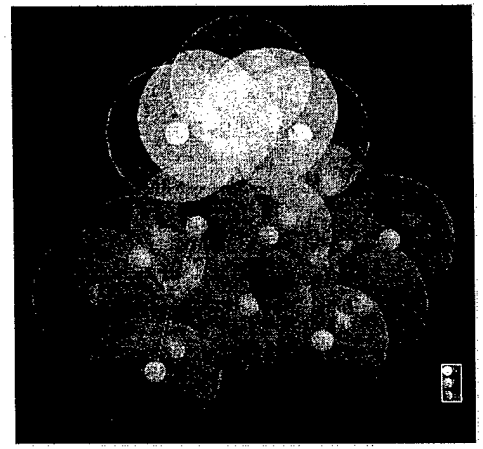
Our research is aimed at increasing propellant Isp by 5 to 50%

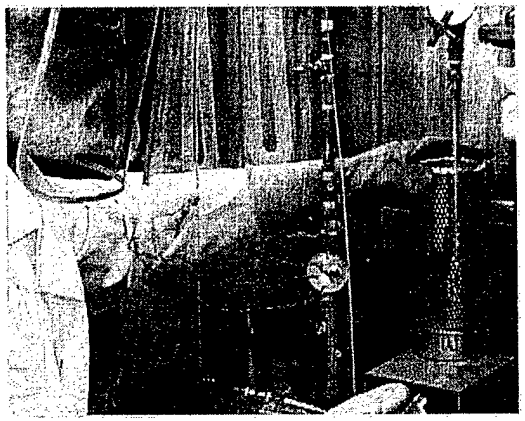
Polynitrogen Project

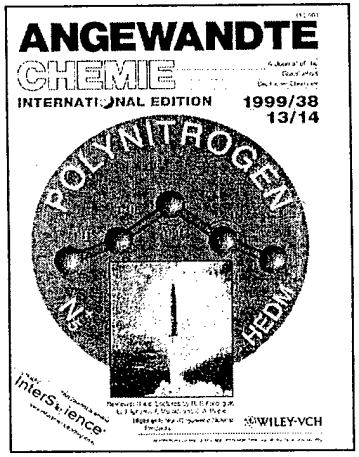
Discover, synthesize, characterize, and scale-up novel, highly energetic polynitrogen allotropes

Modeling and simulation guides the experimental program:

- **Determines which molecules should exist and how energetic they are**
- **Gives information on how to synthesize promising molecules**
- **Provides critical data for identification and characterization of new molecules**



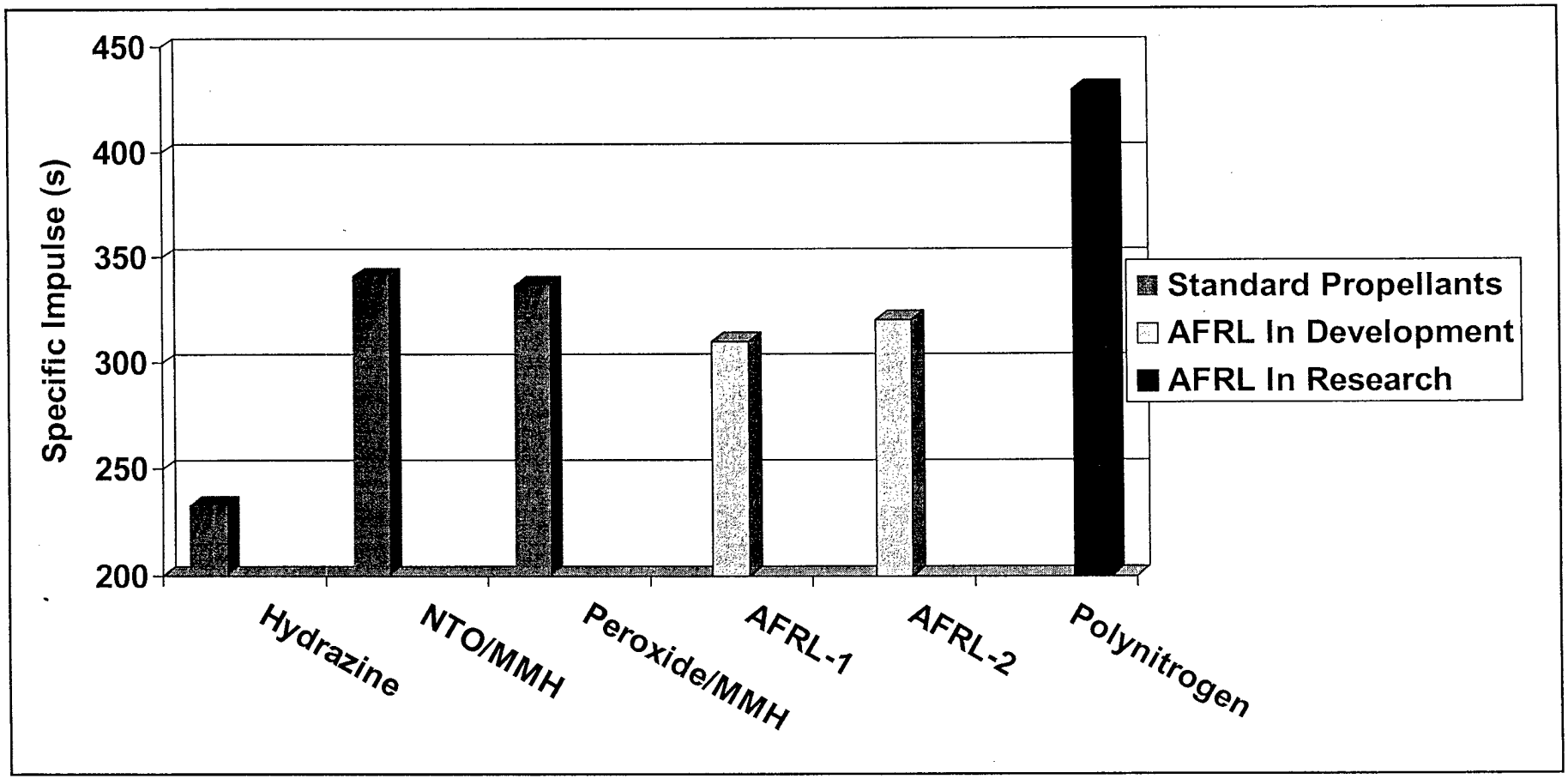




DARPA

Performance of Polynitrogen Monopropellants

The performance of polynitrogens as monopropellants would dwarf that of hydrazine, and would greatly exceed even bipropellants



The Search for New Polynitrogens

- All polynitrogens are unstable with respect to N_2 molecules
- Their activation energy for N_2 elimination is largely determined by the weakest bond in the compound
- Their metastability is enhanced if suitable resonance structures exist:

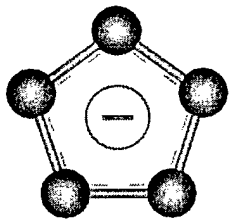
$$[\,|\underline{\overline{N}}\text{–}N\equiv N|\,]^- \longleftrightarrow [\,\diagup\!\overline{N}\!=\!N\!=\!N\!\diagdown\,]^- \longleftrightarrow [\,|N\equiv N\text{–}\underline{\overline{N}}|\,]^-$$

- The double-bond character of the N—N bonds in the azide anion explains its exceptional stability
- How can this stabilization effect be used to our advantage in preparing new compounds?

Pentazolate (N_5^-)?

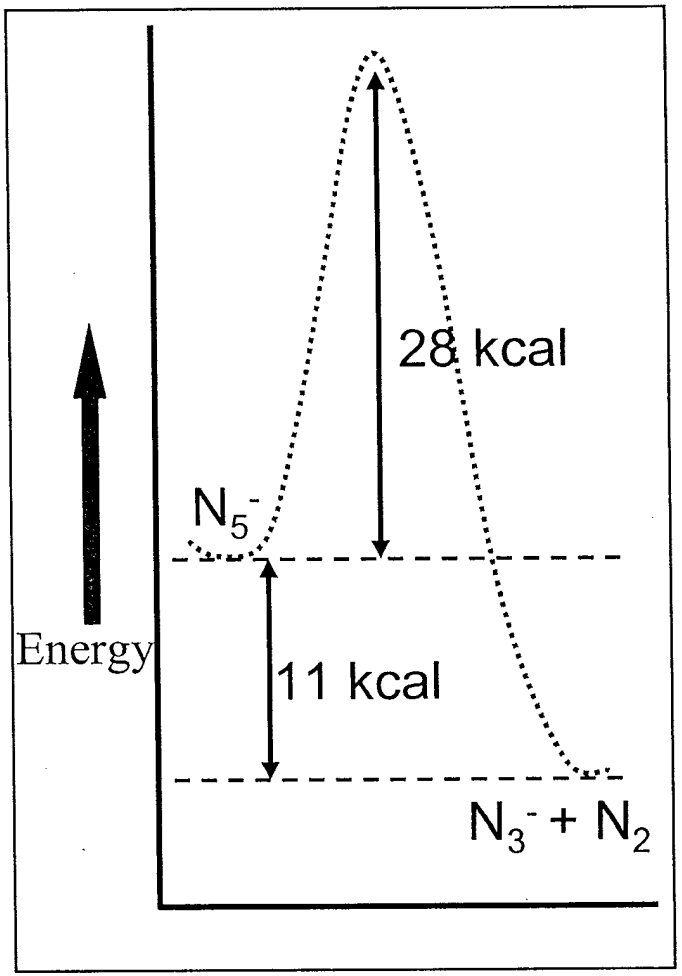
- Substituted pentazoles R-N_5 have been known for decades (R=aryl)
- Cyclic N_5^- is aromatic
- Conversion of the diazonium salt, RN_2^+, to the substituted pentazole ring R-N_5 by the reaction with azide ion, N_3^-, has been demonstrated many years ago by Ugi and Huisgen.
- N_5^- has been recently detected in the gas phase for the first time, using collisional fragmentation (electrospray ion mass spectroscopy).
- Can a chemical route to N_5^- be found? (e.g., can a suitable R group be found for the reaction R-N_2^+ + N_3^- -> R-N_5 -> R^+ + N_5^-?

New Polynitrogen Anions



Pentazole anion (N_5^-)

- *Theoretical calculations show that this anion has a 28 kcal/mole activation energy barrier for decomposition and its decomposition to N_3^- and N_2 is only 11 kcal/mol exothermic*
- *Aryl substituted pentazoles can be isolated as stable compounds only if stored at low temperatures. In methanol, these compounds rapidly decompose at room temperature to form aryl azides and N_2 gas*

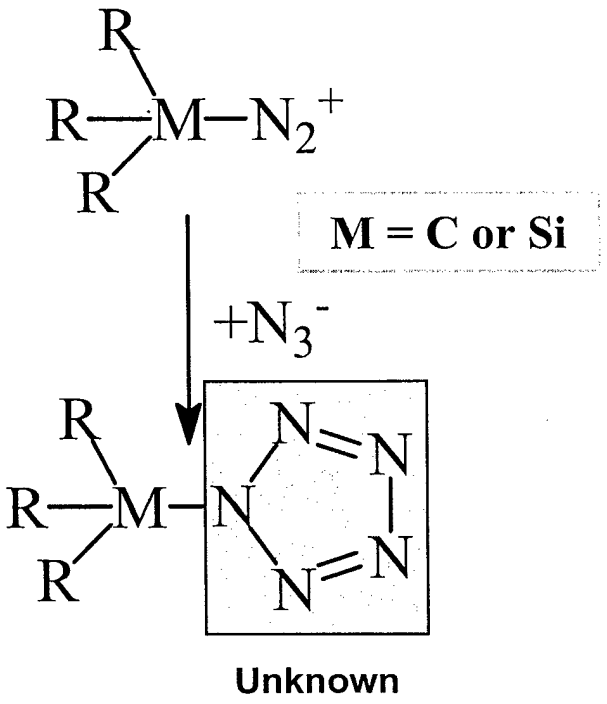


Synthetic Challenge – How do we make These New Anions??

Synthesis of Substituted Pentazoles

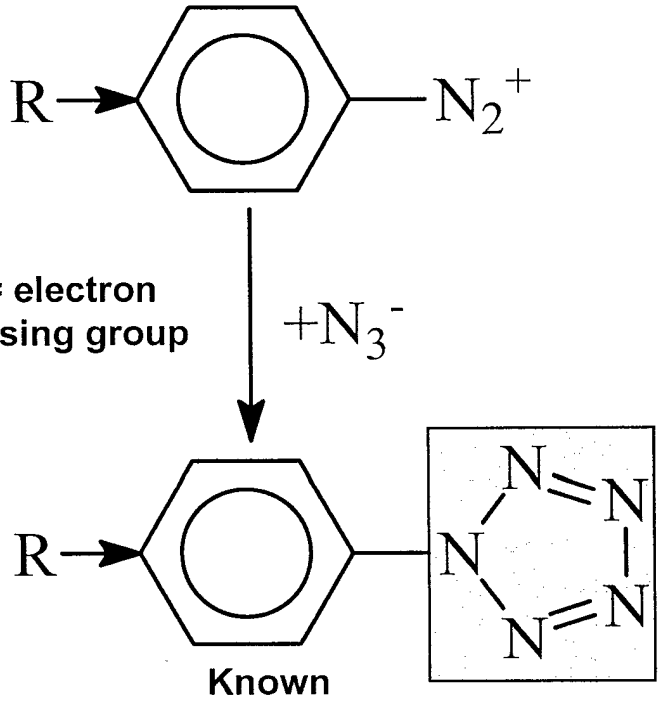
Sources for the Pentazole Anion (N_5^-)

Trityl/Silyl Diazonium Salts



Unknown

Aryl Diazonium Salts



Known

Theoretical Challenge - Can we design and predict viable precursors to N_5^-?

Find a substituent R so that

1. **R-N_2^+ is stable wrt $R^+ + N_2$.**
2. **The R-N bond in R-N_5 is weak, thereby suitable for the reaction R-N_5 + M^+X^- -> $M^+N_5^-$ + R-X**

Approach

Use quantum chemical calculations to predict the stability of R-N_2^+ diazonium salts and the length/strength of the R-N_5 bond.

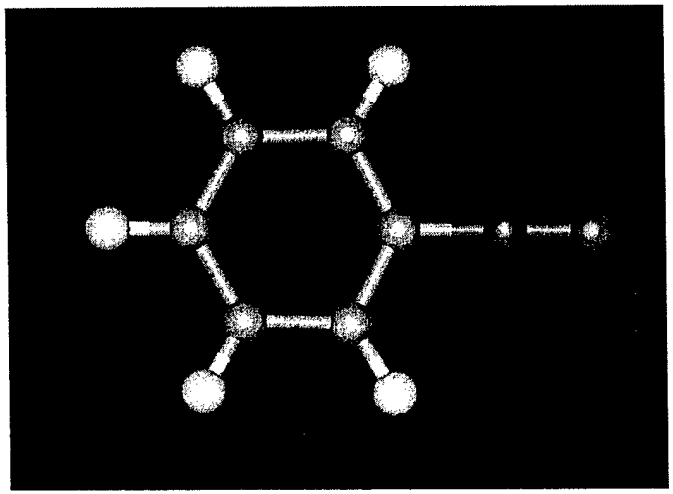
MBPT(2)/6-31G(d) level of theory

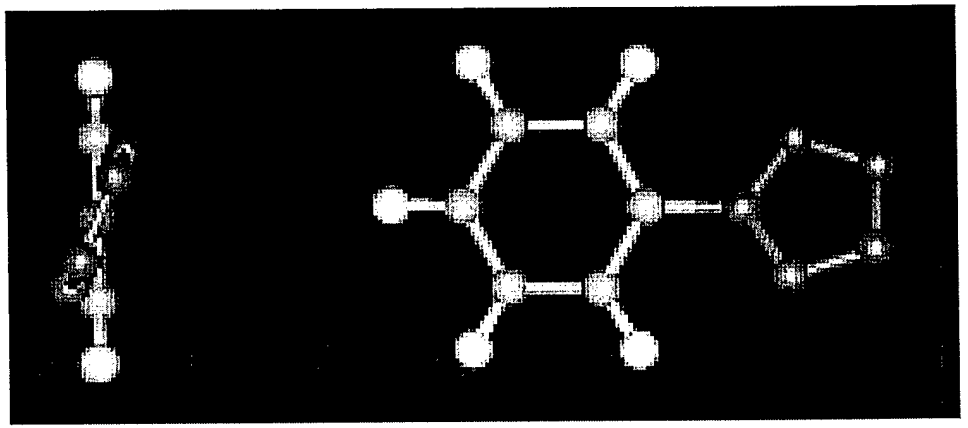
L_3M-N_2^+

M = C, Si

L = F, Cl, CH_3, CF_3, NO_2, phenyl, etc.

Phenyldiazonium -- too stable!





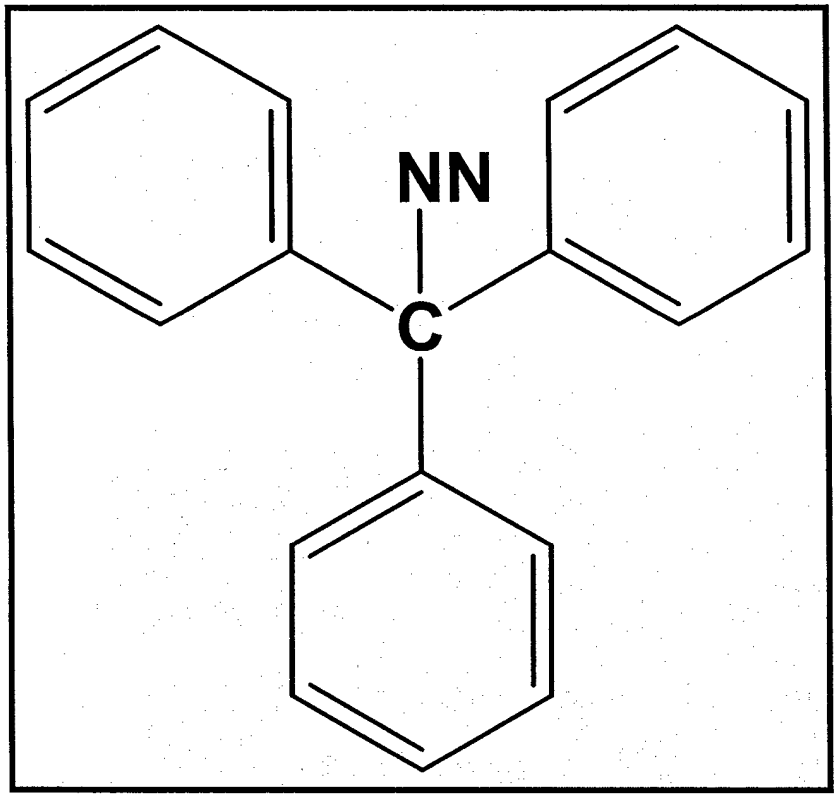
$R(C\text{-}N_2^+) = 1.39$ Å

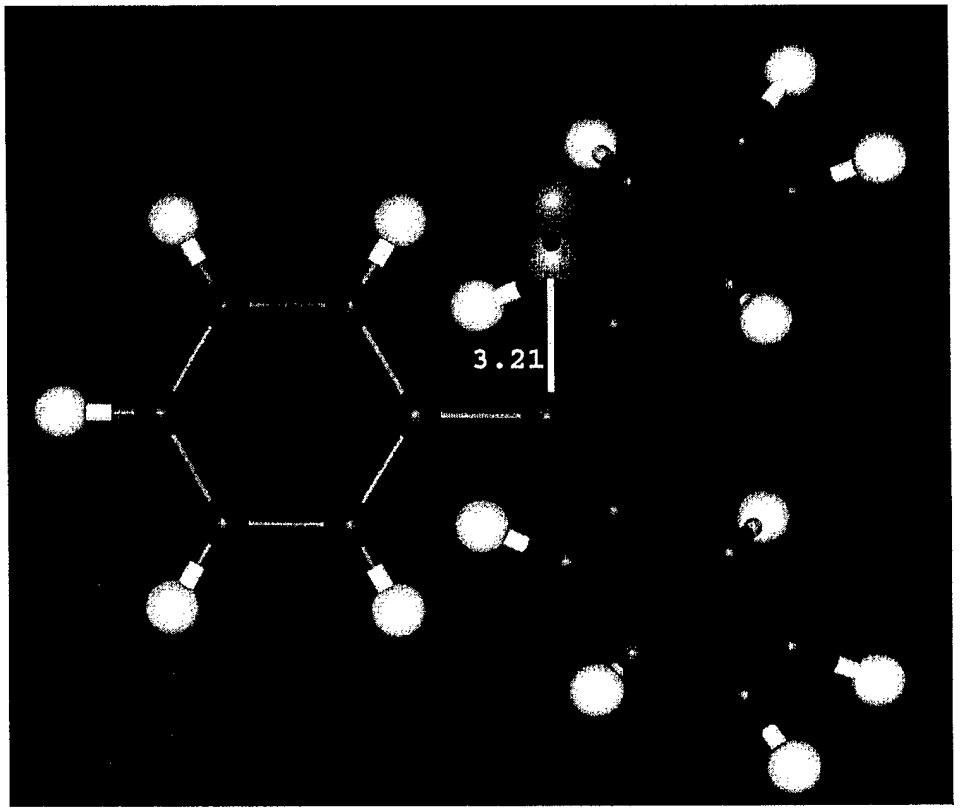
$D_e = 37.9$ kcal/mol

$R(C\text{-}N_5) = 1.43$ Å

Try replacing Ph+ with a more stable cation (Ph_3C^+)...

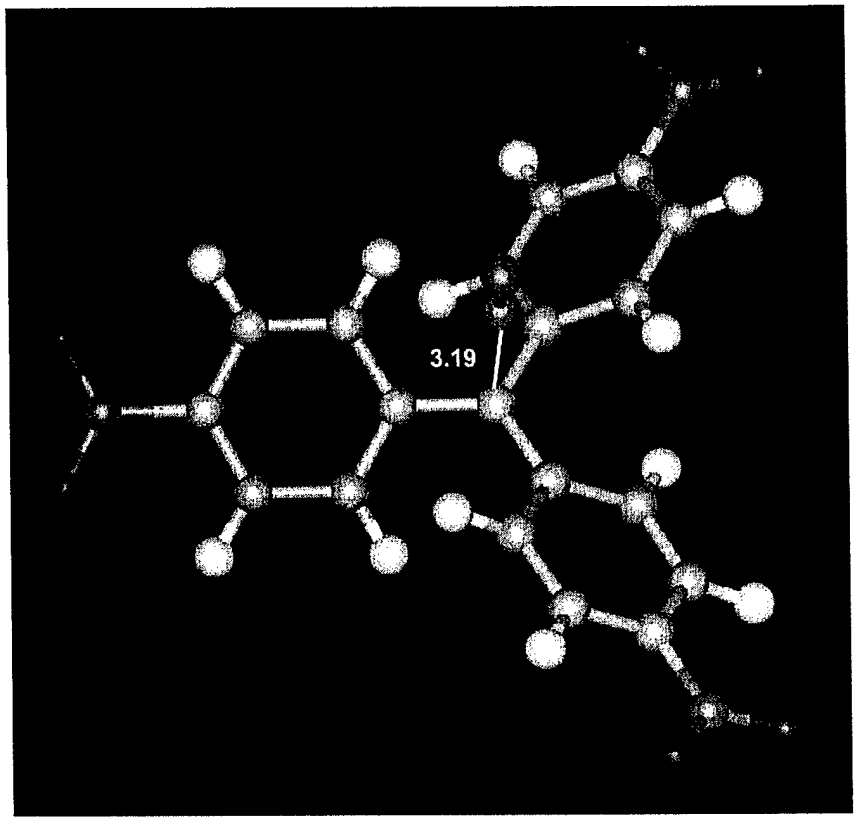
Tritylidiazonium -- unstable!





Trityl cation Ph_3C+ is too stable -- can it be destabilized by placing e-withdrawing groups on the phenyl rings (e.g. NO_2)?

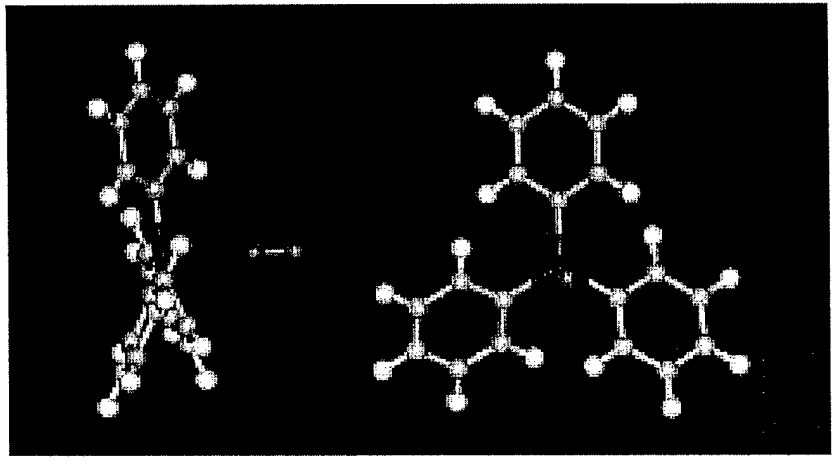
tris(para-nitrophenyl) methyldiazonium

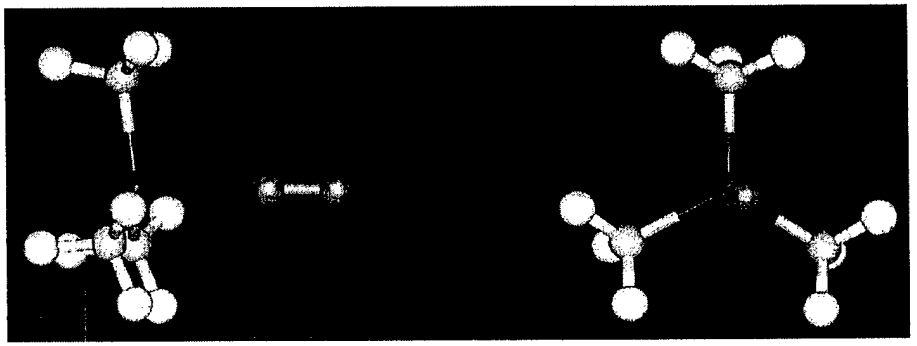


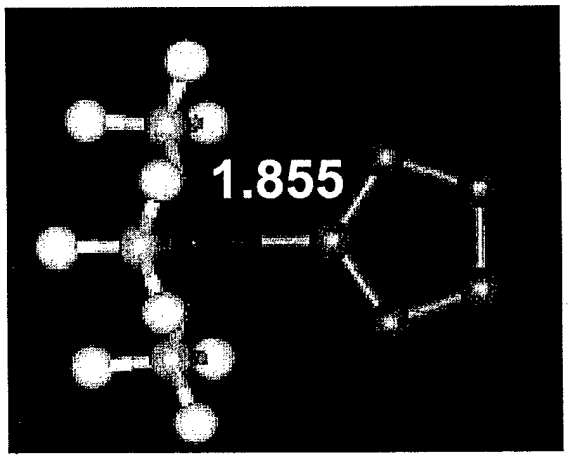
R_3	$R_3C\text{-}N_2^+$ distance(Å)	$D_e(C\text{-}N_2^+)$ (kcal/mol)
3Ph	> 3.0	-3.0
3(pNO_2-Ph)	> 3.0	-3.4

What about some silicon analogues?

R_3	$R_3Si\text{-}N_2^+$ distance(Å)	$D_e(Si\text{-}N_2^+)$ (kcal/mol)
3Ph	> 2.5	-6.0
3Me	2.151	-13.8



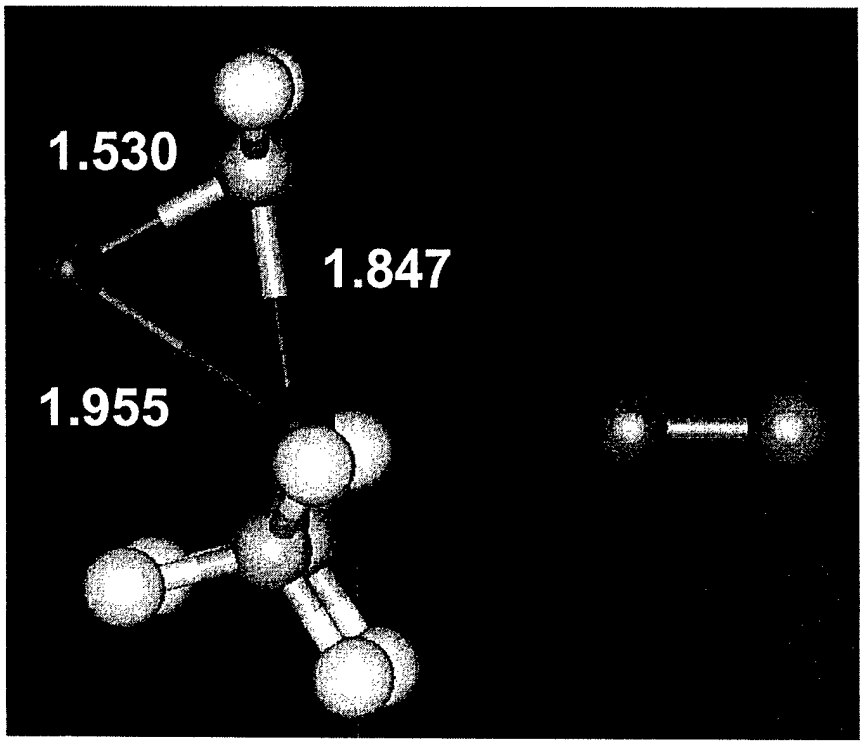


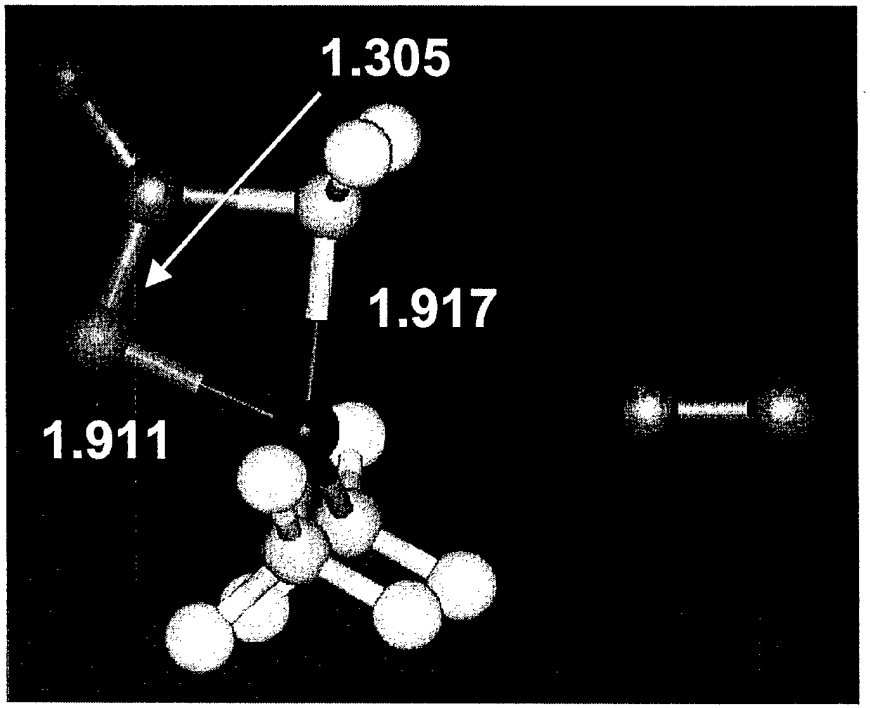


Trimethylsilyl cation looks promising -- can it be "fine-tuned" to give a slightly more stable Si-N bond?

Derivatives of trimethylsilyldiazonium

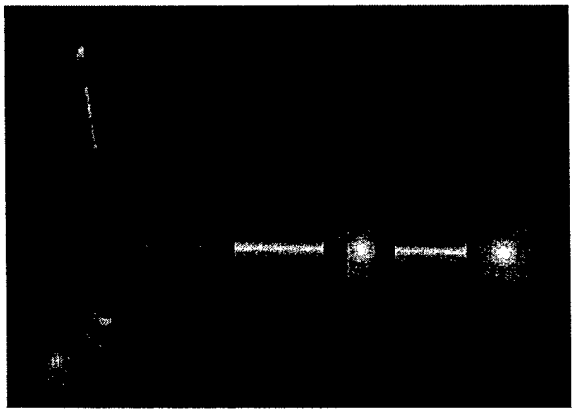
R_3	$R_3Si\text{-}N_2^+$ distance(Å)	$D_e(Si\text{-}N_2^+)$ (kcal/mol)
$2Me,FCH_2$	2.410	-7.4
$2Me,NO_2CH_2$	> 2.5	-5.2

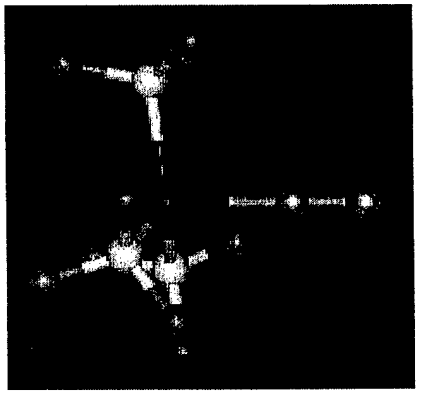


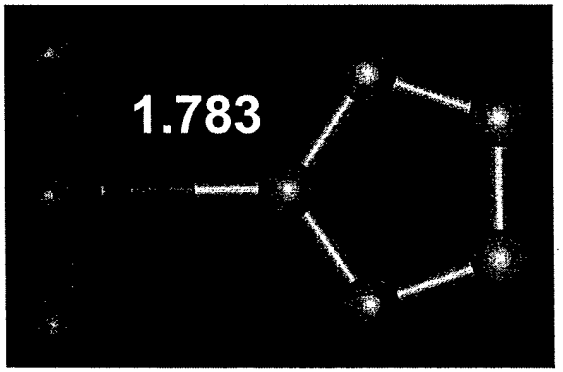


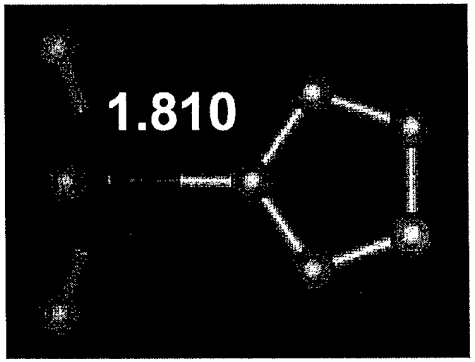
Silicon analogues, continued

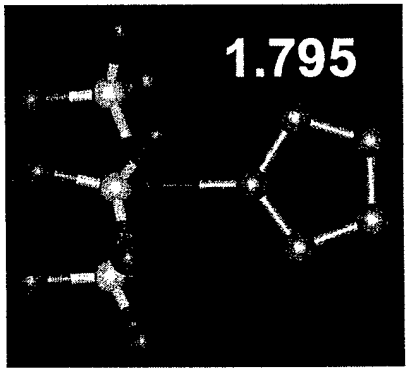
R_3	$R_3Si\text{-}N_2^+$ distance(Å)	$D_e(Si\text{-}N_2^+)$ (kcal/mol)
3F	1.973	-33.4
3Cl	2.125	-14.5
$3CF_3$	1.994	n/a











Conclusions

- Trityldiazonium ($Ph_3C\text{-}N_2^+$) and its tris(para-NO_2) analogue are predicted to be unstable wrt dissociation of N_2
- $Ph_3Si\text{-}N_2^+$ is also predicted to be unstable wrt dissociation of N_2
- $Me_3Si\text{-}N_2^+$ and $Cl_3Si\text{-}N_2^+$ are marginally stable (D_e ~ 14 kcal/mol; R(Si-N) ~ 2.1 Å)
- Of the silyl derivatives considered, $F_3Si\text{-}N_2^+$ is the most stable (D_e = 33.4 kcal/mol; R(Si-N_2^+) = 1.97 Å)
- Secondary (i.e., not directly bonded to Si) electronegative groups such as F and NO_2 interact strongly with Si in silyldiazonium cations, leading to displacement of N_2

Future/ongoing work

- Calculation of the structures and stabilities of $Me_xF_yCl_zSi\text{-}N_2^+$ and $Me_xF_yCl_zSi\text{-}N_5$
- Calculation of the reaction enthalpies $R\text{-}N_5 + M^+X^- \rightarrow M^+N_5^- + R\text{-}X$
- Other high-nitrogen/polynitrogen species (e.g. $Fe(N_5)_2$)

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New Materials Design Challenge Project

Aeronautical System Center

AFFTC Distributed Center

Army HPC Research Center

Common HPC Software Support Initiative

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